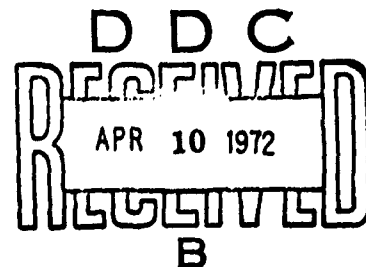


AD 739639

Ellipsometric-Potentiostatic Studies of Steel Corrosion: Oxide Film Development and Effects of Inhibitors*

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Abstract

Simultaneous ellipsometric-potentiostatic measurements were used to study film development on mild steel in borate-boric acid buffer solutions at pH 7.4, with and without 0.005M and 0.0025M KCl. Effects of pre-adsorbed films of barium dinonylnaphthalene sulfonate were also determined. Coulometric and ellipsometric film thicknesses of the anodic films agreed reasonably well. Discrepancies increased when pitting occurred because of surface roughening. Chloride ion reduced the passive range and caused increased corrosion at a lower potential. Pre-adsorbed sulfonate films desorbed rapidly under anodic polarization, but were stable for 0.1 to 0.2 volt cathodic. The initial corrosion rate for the bare steel, determined by the Tafel extrapolation and linear polarization methods, was 4 mpy. The pre-adsorbed sulfonate film reduced the corrosion rate to 1 mpy.

Polar organic corrosion inhibitors are used extensively in corrosion preventives and lubricants. These inhibitors act by adsorption at anodic or cathodic sites, or by nonspecific adsorption, with the long nonpolar groups of the inhibitor molecules covering adjacent areas. The nonpolar groups also hold oil molecules in the surface layer to aid in forming a barrier to corrosive substances.¹ Electrostatic forces are frequently involved in the adsorption of these organic inhibitors. The effects of the surface charge of the metal on inhibitor adsorption and efficiency have been discussed by Foroulis.² That discussion was centered on inhibitors for acid corrosion of ferrous and other metals. The present work was undertaken in an attempt to investigate the effects of electrical polarization on organic inhibitors in neutral or almost neutral solution.

Experimental Procedure

The basis for the experimental techniques used was provided by Kruger and Calvert³ and by Nagayama and Cohen.⁴ Initially, the passive-active process for mild steel in a salt solution was determined. Then, polarization experiments were performed on steel with pre-adsorbed films of a sulfonate-type inhibitor. Corrosion currents were determined by the Tafel extrapolation and the linear polarization methods.

Apparatus

A diagram of the experimental setup is shown in Figure 1. The potentiostat used was a Model 61RH Wenking, with 3000 milliamperes current range and 2000 millivolts maximum potential. The ellipsometer was an O. C. Rudolph and Sons, Inc., Model 436/200B instrument with a photoelectric null meter. The Pyrex glass cell contained a platinum wire counter electrode, the steel working elec-

trode, two optically flat windows, and a Luggin capillary connected through a salt bridge to the saturated calomel electrode (SCE).

Materials

Solutions used were prepared from de-ionized water with specific resistance 4.5×10^6 ohms. Reagent grade boric acid and sodium borate were used to prepare buffer solutions with pH 7.4, as described by Kruger and Calvert.³ Reagent grade potassium chloride was used to prepare 0.0025M and 0.005M chloride solutions in the pH 7.4 buffer. The solutions were de-aerated by bubbling 99.996% He through them for two hours before use.

The working electrode was a cylinder of AISI 1020 steel 4.8 mm in diameter and 12 mm long, cut from a rod. The steel had the following analysis (percentages): C, 0.22; Mn, 0.47; Si, 0.18; Cu, 0.04; P, 0.01; and S, 0.02. A shrinkable Teflon sleeve⁵ and glass tube held the steel electrode in a ground glass joint for insertion in the cell. Only the circular cross section of the electrode was exposed to the solution. When the electrode and the solution were in place, the cell was covered with a Teflon lid with openings for the He gas inlet, the platinum electrode, and the Luggin capillary. Basic barium dinonylnaphthalene sulfonate (BaDNNS) (Vanderbilt), and sorbitan monooleate (J. T. Baker, technical grade) were used to form pre-adsorbed films on the steel surface.

Procedure

The steel electrode was mechanically polished with 600 grit silicon carbide and 1 micron alumina. It was then electropolished in an acetic-perchloric acid mixture according to the procedure of Nagayama and Cohen,⁴ washed with methanol, dried in a stream of dry nitrogen, and placed in the cell. Solutions were added by means of a pipet; exposure to air occurred at this time. A stream of He was passed over the solution in the cell during the polarization experiments. All measurements were made at

*Presented at the Corrosion Research Conference, National Association of Corrosion Engineers, March 22-26, 1971, Chicago, Ill. Submitted for publication March, 1971.

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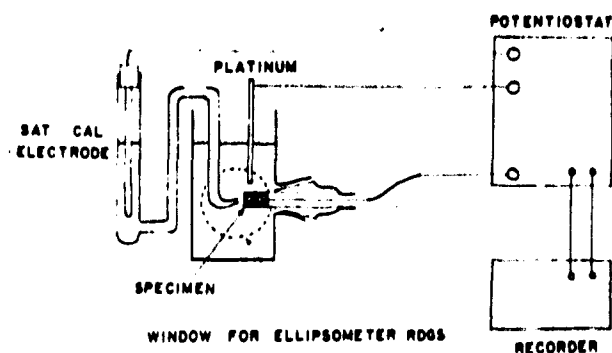


FIGURE 1 - Test cell and experimental setup.

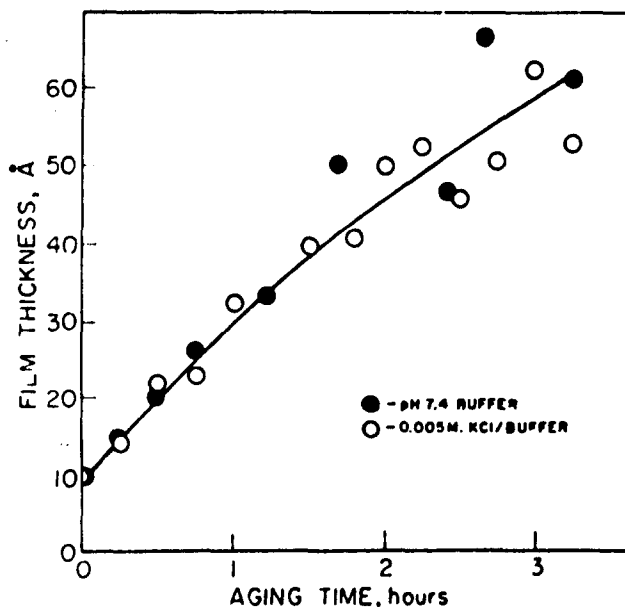


FIGURE 2 - Rate of formation of oxide films on steel aging in pH 7.4 buffer solution with and without chloride.

room temperature, $24 \pm 1^\circ\text{C}$ (75°F). All voltages reported here are versus the saturated calomel electrode.

Several types of experiments were conducted on the immersed steel electrodes. These experiments were as follows:

1. The existing corrosion film that formed immediately after electropolishing was reduced cathodically until the rest potential and ellipsometer readings stabilized. Film thicknesses were calculated from the ellipsometer readings by means of the McCrackin computer program.⁶ The angle of incidence was 70° , and the wave length 5461\AA . A complex film refractive index of $2.5-0.3i$ was assumed³ in these calculations.

2. The steel electrode was allowed to age for several hours in the solution without application of a control potential. The purpose of this aging was to obtain films of known thickness to compare corrosion rates and effects of inhibitors.

3. The steel electrode was anodically polarized to develop passive films on the steel surface. The thicknesses of these films were determined from ellipsometer measurements and from current-time data. For the latter calculations, a roughness factor of 1.3 and corrosion film density of 5 gm/cm^3 were assumed.³ Effects of cathodic polarization were also determined.

4. Films of BaDNNS and BaDNNS plus sorbitan monooleate were pre-adsorbed on the steel surfaces and subjected to potentiostatic polarization and ellipsometric observations. These BaDNNS films were adsorbed either from the concentrated commercial product or from 5% solutions in redistilled isooctane (ASTM knock test grade) for periods ranging from 2 to 16 hours. The films were rinsed three times with fresh portions of isooctane before the electrode was placed in the cell. Mixtures of equal parts of BaDNNS and sorbitan monooleate were used in a similar manner to form mixed films.

Results and Discussion

Cathodic Reduction

Cathodic reduction of the steel in the buffer solution, without chloride, gave changes in the optical parameters Δ , or phase retardation, and ψ , or relative amplitude reduction, corresponding to a calculated average film thickness of $10 \pm 2\text{\AA}$ (95% confidence limits). The complex refractive index calculated for this cathodically reduced steel surface was $2.73 (\pm 0.06) - 3.55 (\pm 0.10)i$. Attempts to reduce the existing film in solutions containing 0.0025M or 0.005M chloride resulted in no definite change in Δ or ψ ; this indicated that the film was not reduced in these solutions.

Aging

Results of the aging process for the steel electrode are shown in Figure 2. Note that the thicknesses begin at 10\AA , the average thickness of the film formed after electropolishing. The average corrosion film thickness on the steel surface after three hours was 60\AA . As indicated by the graph, chloride ion in the concentration used had little or no effect on the formation of these films in the first three hours.

Anodic and Cathodic Polarization

Anodic and cathodic potentiostatic curves were obtained on the steel in the buffer solution and in the buffer with 0.0025M KCl. A plot of the current densities at one minute after application of each potential is shown in Figure 3. The curves show that the span of the passive region is reduced, as expected, by the chloride ions. Solutions containing 0.005M chloride gave similar results.

Film thicknesses obtained after one hour of anodic polarization at several overvoltages are shown in Figure 4. The rest potential was -0.7 volt. These curves show an expected close correlation with the current-potential data shown in Figure 3. Pitting of the steel surface could be observed with the ellipsometer when bright spots appeared in the field of illumination. The film thicknesses given in Figure 4 near the pitting region are, without any doubt, considerably in error because of surface roughening.

Kruger and Calvert³ reported film thicknesses of anodic films on large grained purified iron samples to be $20-30\text{\AA}$ at pH 7.4 in the overpotential range of 0.7 to 1.5 volts. The data in Figure 4 show a more rapid increase in film thickness for the mild steel specimens over the same potential range.

Coulometric and ellipsometric film thicknesses of some of the anodic films plotted in Figure 3 are compared in

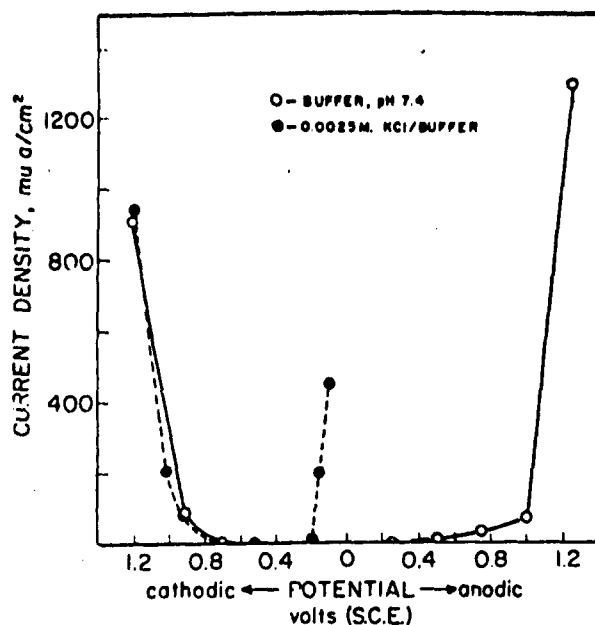


FIGURE 3 - Current densities after one minute-polarization curves for mild steel in buffer and 0.0025M KCl/buffer solutions.

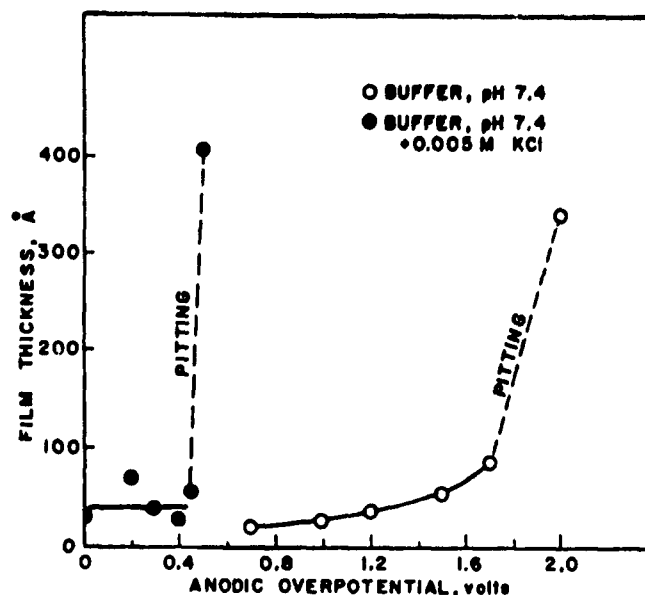


FIGURE 4 - Film thickness after one hour-anodic overpotential relationships for steel in pH 7.4 buffer solution and in 0.005M KCl/buffer.

Table 1. These film thicknesses were calculated from coulometric and ellipsometric data obtained during ten minutes of anodic polarization. Good agreement exists between the two types of measurement for the thinner films, but this is not so for the thicker films. The lack of agreement for the thicker films can be explained by the increasing roughness of the steel surface.⁷

Inhibitor Films

Another series of experiments was performed to determine the effects of polarization on uninhibited and inhibited steel surfaces. Polarization rates in these experiments were 10 mv per 30 seconds after an initial 5 mv polarization for 30 seconds. Results are plotted in Figures 5 and 6.

Some discussion of the meaning of the changes in Δ may be necessary for an interpretation of these graphs. A decrease in Δ can indicate the growth of an oxide or corrosion film. An increase in Δ can mean (1) a decrease in film thickness of an oxide or corrosion film, (2) the development of a film with refractive index less than that of the medium, e.g., hydrogen, or (3) a roughening of the

surface. These and other possibilities have been discussed by Kruger.^{3,7} The interpretations of the present data are given in the following paragraphs.

The decrease in Δ shown by Curve 1 of Figure 5 indicates the formation of an anodic film on the unaged steel surface. The change in Δ for an aged surface polarized at the same rate is shown by Curve 2. The slower decrease in Δ for Curve 2 compared with Curve 1 may have at least two explanations:

First, if the aging film consisted primarily of ferrous ion, then the current flow during polarization would be used mainly to oxidize the ferrous to ferric ion. The film thickness, and therefore Δ , would change little during this process. Second, some of the charge passed may correspond with the dissolution of ferrous ion at the same rate at which it is formed from the underlying metal. Nagayama and Cohen⁴ showed that ferrous ion dissolves in the region below -200 mv (SCE) during anodic polarization of pure iron. Both of the processes probably occurred here. The sharp increase in Δ at about -0.87 volt under cathodic polarization, shown in Curve 3 of Figure 5, is best explained by hydrogen formation. This conclusion is

TABLE 1 - Anodic Films on Steel: Comparison of Coulometric and Ellipsometric Film Thicknesses

| Experiment | Anodic Over-Potential, Volts | $Q^{(1)}$ Coulombs/cm ² | Film Thickness, Δ | |
|------------|------------------------------|---------------------------------------|--------------------------|---------------|
| | | | Coulometric | Ellipsometric |
| 88 | 0.70 | 0.0053 | 23 | 19 |
| 87 | 0.95 | 0.0062 | 27 | 26 |
| 50 | 1.20 | 0.0110 | 47 | 36 |
| 51 | 1.45 | 0.0344 | 148 | 52 |
| 52 | 1.70 | 0.0293 | 126 | 88 |

⁽¹⁾ Q - total electric charge used in film formation, obtained by graphical integration of current time curves.

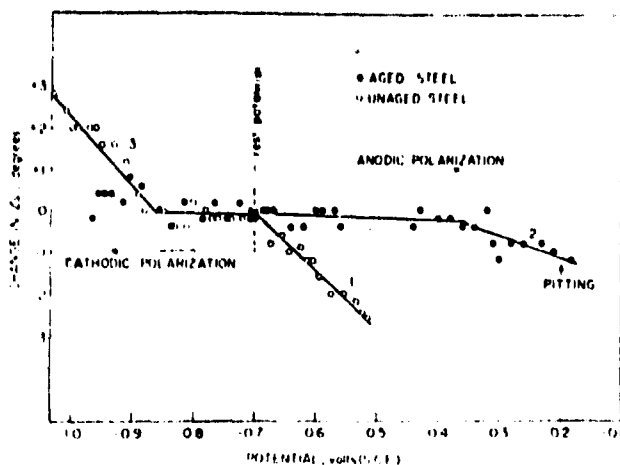


FIGURE 5 - Change of phase retardation with potential for mild steel in 0.005M KCl/buffer solution.

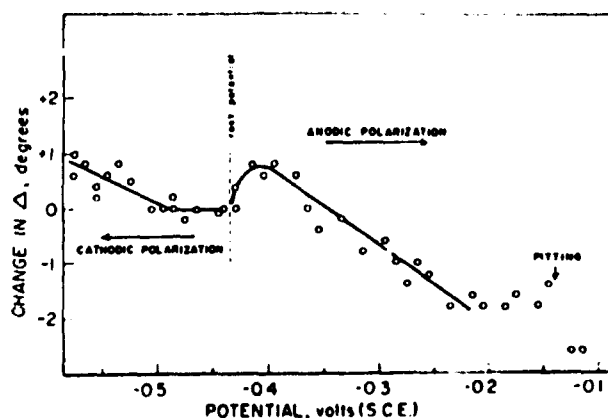


FIGURE 6 - Change of phase retardation with potential for unaged steel surface with pre-adsorbed BaDNNS in 0.005M KCl/buffer solution.

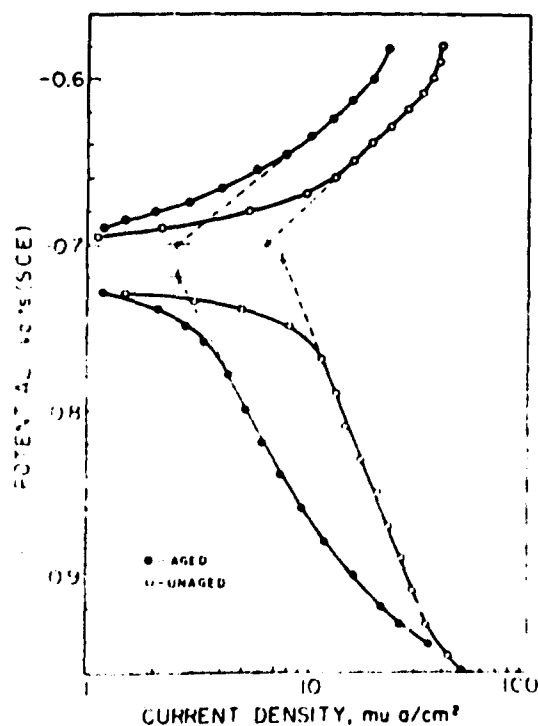


FIGURE 7 - Anodic and cathodic polarization curves for mild steel in 0.0025M KCl/buffer solution.

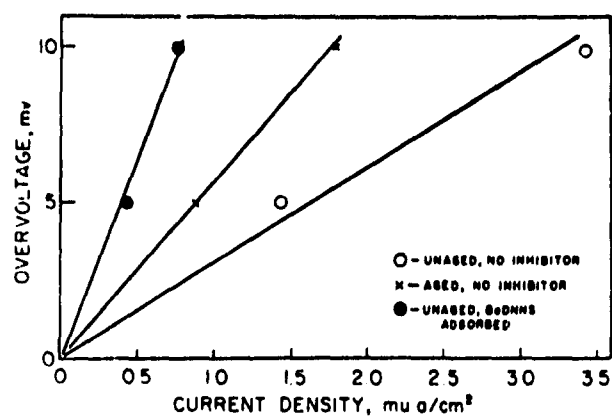


FIGURE 8 - Linear polarization curves for mild steel with and without BaDNNS adsorbed in 0.0025M KCl/buffer solution.

reinforced by the fact that the Δ value dropped almost immediately to within about 0.4° of its initial value when the applied potential was interrupted.

A typical curve for the behavior of adsorbed BaDNNS is shown in Figure 6. The rest potentials of the steel electrodes containing pre-adsorbed films varied from -0.25 to -0.45 volt, compared with rest potentials of -0.68 to -0.70 volt for the bare steel. The sulfonate film appeared to desorb immediately on application of potential in the anodic direction and, after the desorption had occurred, the anodic film developed. Pitting of the electrode then occurred near the pitting potential of bare steel in the chloride solution. Under cathodic polarization, the film appeared to remain intact for a span of about 100 mv. For the BaDNNS films and co-adsorbed BaDNNS plus sorbitan monooleate, desorption took place between -0.4 to -0.5 volt on cathodic polarization. Whenever the film began to desorb under cathodic polarization, the rest potential shifted to that for bare steel because no source of inhibitor was available to replenish the film.

Corrosion rates were determined for the bare steel and for the steel with pre-adsorbed inhibitor. Polarization curves for the steel in 0.0025M KCl/buffer solutions are shown in Figure 7. With an approximate factor of 0.5 mpy for $1 \mu\text{A}/\text{cm}^2$ corrosion current, the Tafel extrapolation method gives corrosion rates of 3.2 mpy for the unaged specimen with 10A initial film and 1.2 mpy with 60A initial film. The same polarization technique could not be used on the electrodes with pre-adsorbed inhibitors because the rapid desorption of the inhibitor allowed the rest potential to shift. Therefore, the linear polarization method was used to determine the corrosion rate of the inhibited surfaces.

A plot of the results of linear polarization at 5 and 10 mv is shown in Figure 8. Each point is an average of three determinations. Corrosion currents were then estimated from the equation

$$\frac{\Delta E}{\Delta I} = \frac{0.026}{I_c} \quad (1)$$

where $\Delta E/\Delta I$ = slope of linear polarization curve and I_c = corrosion current.

Equation (1) is derived from the Stern-Geary equation⁸ on the assumption of average beta values.⁹ Corrosion rates obtained by use of Equation (1) and the data of Figure 8 are as follows: For unaged steel, 4.4 mpy; for aged steel, 2.4 mpy; and for unaged steel with BaDNNS adsorbed, 1.0 mpy. The agreement of these data, for the bare steel, with the corrosion rates given by the Tafel extrapolation is good when the approximate nature of Equation (1) is considered.

Another comparison of rates of corrosion may be attempted between the data of Figure 2 and those given by the Tafel extrapolation of Figure 7. The slope of the curves in Figure 2 gives a rate of formation of film of 20Å/hr initially, and 10Å/hr at three hours. The corresponding rates of metal conversion to corrosion film would be 12.5Å/hr and 6.25Å/hr, respectively, with the assumption of a metal to corrosion film density ratio of 8:5. The corrosion rates converted to mpy would be 0.44 and 0.22, respectively. The corrosion rates given by the Tafel extrapolation are over seven times these rates. The difference is the rate of dissolution of the metal. Approximately 14% of the metal remains as corrosion film; the remainder passes into solution under the experimental conditions. The data of Nagayama and Cohen⁴ also indicate that considerable metal dissolution occurs below -200 mv.

Conclusions

For the system studied, the linear polarization and Tafel extrapolation methods give corrosion rates that are in reasonably good agreement.

Pre-adsorption of BaDNNS corrosion inhibitor causes a

shift of initial rest potential toward anodic values and a decrease in the corrosion rate.

Addition of small concentrations of chloride ion reduces the passive range and accelerates the corrosion of steel at a lower potential.

BaDNNS films desorb under anodic polarization, but are stable over a narrow range of cathodic potentials. This is in accord with the inefficiency of this type of inhibitor in salt media. The inhibitor apparently desorbs from anodic areas, leaving them open to pitting attack by chloride ion.

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